university of groningen

University Medical Center Groningen

University of Groningen

Reply to the comments by Morrison

ten Brinke, G. ; Karasz, F. E.

Published in:
The Journal of Chemical Physics

DOI:
10.1063/1.445289

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1983

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
ten Brinke, G., & Karasz, F. E. (1983). Reply to the comments by Morrison. *The Journal of Chemical Physics*, *78*(7), 4792-4792. https://doi.org/10.1063/1.445289

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 05-05-2023

Reply to the comments by Morrison[a)]

G. ten Brinke and F. E. Karasz

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003
(Received 29 November 1982; accepted 23 December 1982)

Our discussion[2] within the framework of scaling theory showed also clearly that certain qualitative features are essentially a consequence of the stability criterion. In addition to this the symmetry embodied in the scaled equation of state was shown to be essential for the derivation of the explicit Eq. (7). We restricted ourselves to the phase behavior in an isobaric plane, but a similar analysis can be given for an isothermal plane, resulting in a relation between the volume of mixing and the type of phase behavior in this plane, i.e., upper or lower critical solution pressure. The qualitative results relating the signs of the enthalpy of mixing and the volume of mixing to the type of phase behavior follow, in accordance with Morrison's main conclusion, also from a thermodynamic analysis given by Rowlinson.[3,4]

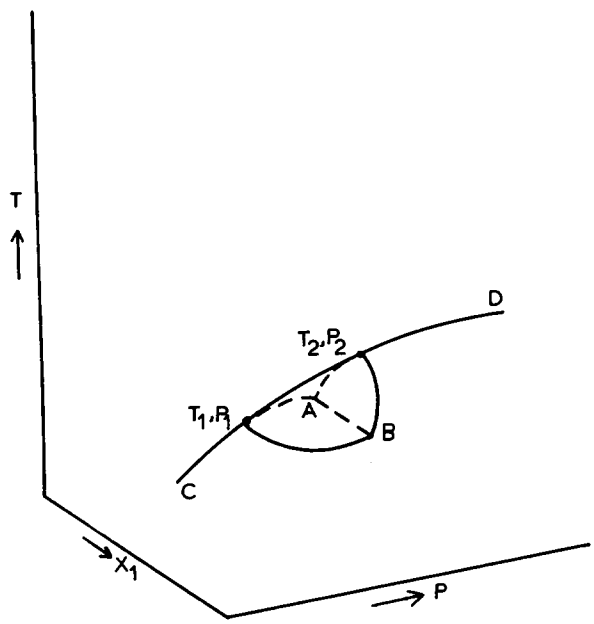

FIG. 1. Schematic three-dimensional P,T,x_1 diagram showing a critical line CD. A and B are the points of intersection of the coexistence curve in the isothermic plane through the critical point T_1,P_1 and the coexistence curve in the isobaric plane through the critical point T_2,P_2. The drawing is for the particular case of UCST behavior with $d\mathrm{UCST}/dP>0$.

The scaling analysis for an isothermal plane results in an expression for the volume of the mixture analogous to Eq. (7) of our previous note.[2] Combining expressions (3) and (7) of that note with the corresponding ones for an isothermal plane, as indicated in Fig. 1, results in the following equation for the pressure dependence of the critical temperature T_1:

$$\frac{dT_1}{dP}=\lim_{(T_2,P_2)\to(T_1,P_1)} T_1\frac{(\partial V/\partial x_1)_A-(\partial V/\partial x_1)_B}{(\partial H/\partial x_1)_A-(\partial H/\partial x_1)_B},$$

where H, V, and x_1 denote the enthalpy, the volume, and the concentration of component 1. The salient part of this equation can also be written as

$$\lim_{x_{1A}\to x_{1B}}\left(\frac{\Delta(\partial V/\partial x_1)}{\Delta x_1}\right)_P\Big/\left(\frac{\Delta(\partial H/\partial x_1)}{\Delta x_1}\right)_T,$$

where $\Delta x_1=x_{1A}-x_{1B}$. Since the numerator and denominator are the operational definitions of the second derivatives of the volume and enthalpy, the given expression for dT_1/dP is equivalent to the one given by Myers *et al.*[5]

[a)]Reference 1.

[1]G. Morrison, J. Chem. Phys. 78, 4790 (1983).
[2]G. ten Brinke and F. E. Karasz, J. Chem. Phys. 77, 5249 (1982).
[3]J. S. Rowlinson, *Liquid and Liquid Mixtures*, 2nd ed. (Plenum, New York, 1969), p. 146.
[4]Y. Suzuki, Y. Miyamoto, H. Miyayi, and K. Asai, J. Polym. Sci. Lett. 20, 569 (1982).
[5]D. B. Myers, R. A. Smith, J. Katz, and R. L. Scott, J. Phys. Chem. 70, 3341 (1966).

Hypervirial calculations of Morse oscillator matrix elements

A. Requena, R. Peña, and J. Zúñiga

Department of Physical Chemistry, University of Murcia, Murcia, Spain
(Received 11 October 1982; accepted 22 December 1982)

In a recent paper, Huffaker and Tran[1] propose the use of the standard techniques of the factorization method[2] to obtain formulas for matrix elements of powers of the quantity

$$y=1-\exp(-aq) \tag{1}$$

for bound levels of a Morse oscillator. Expressions for diagonal and off-diagonal matrix elements of y, y^2, y^3, and

 0021-9606/83/074792-01$2.10 © 1983 American Institute of Physics

Downloaded 15 Dec 2005 to 129.125.25.39. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp